DESCRIPTION

SOLID ELECTROLYTIC CAPACITOR AND FABRICATION METHOD
THEREFOR

TECHNICAL FIELD

The present invention relates to a solid
electrolytic capacitor and a fabrication method therefor.
More particularly, the invention relates to a solid
electrolytic capacitor comprising an anode formed of at
least one metal selected from tantalum, niobium, titanium
and tungsten, a dielectric layer formed on the anode, and
an electrolytic layer and a cathode disposed on the
dielectric layer, characterized in that the cathode is
improved and an equivalent series resistance (ESR) in high
frequency regions is decreased.

BACKGROUND ART

Solid electrolytic capacitors are conventionally
used for personal computers and so on.

Recently, an instant supply of current to a circuit
has been required because of increase in frequency of CPUs
for use in personal computers. Therefore, development of a
solid electrolytic capacitor featuring a decreased
equivalent series resistance in high frequency regions has
been demanded.

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As such solid electrolytic capacitors, solid electrolytic capacitors including an anode formed of a metal, such as tantalum and so on, a dielectric layer of an oxide of such a metal formed on the anode, and an electrolytic layer and a cathode deposited on the dielectric layer are generally used.

As the cathode of such solid electrolytic capacitors, two layers of a carbon layer and a silver layer deposited on the electrolytic layer are generally used.

However, the cathode of the two layers of the carbon layer and the silver layer has a problem as follows. Because a contact resistance between the carbon layer and the silver layer is increased due to differences in properties between the carbon layer and the silver layer, the equivalent series resistance in the high frequency regions is increased.

Therefore, for example, JP-A-10-242000 discloses a solid electrolytic capacitor including the cathode comprising three layers of a carbon layer, a mixed layer of carbon and silver and a silver layer formed on an electrolytic layer for the purpose of decreasing the equivalent series resistance in the high frequency regions.

However, according to results of examinations made by inventors of the present invention, in the case of forming the three layers of the carbon layer, the mixed

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layer of carbon and silver, and the silver layer as the cathode on the electrolytic layer as mentioned above, the contact resistance between the mixed layer of carbon and silver and the silver layer was increased and it was still impossible to sufficiently decrease the equivalent series resistance in the high frequency regions.

DISCLOSURE OF THE INVENTION

The present invention is made in order to solve the aforementioned problems. Also, it is an object of the invention to decrease a contact resistance and so on to obtain a solid electrolyte capacitor with a decreased equivalent series resistance in high frequency regions.

According to the invention, a solid electrolytic capacitor comprises an anode formed of at least one metal selected from tantalum, niobium, titanium and tungsten and a dielectric layer, an electrolytic layer and a cathode disposed on the anode, wherein the cathode comprises a mixed layer containing a first material consisting of silver particles having an average particle diameter (median diameter) of not less than 2 μm, a second material consisting of conducting carbon particles and/or silver particles having an average particle diameter (median diameter) of 1 μm or less and a binding agent.

As the aforementioned solid electrolytic capacitor, in a case where the mixed layer containing the first material consisting of the silver particles having the median diameter of not less than 2 μm, the second material consisting of the conducting carbon particles and/or the silver particles having the median diameter of 1μm or less and the biding agent is formed as the cathode on the electrolytic layer, the particles of the second material consisting of the conducting carbon particles and/or the silver particles having the median diameter of 1 μm or less enter spaces between the particles of the first material consisting of the silver particles having the median diameter of not less than 2 μm, so that conductivity in the mixed layer is improved and adhering property between the mixed layer and the electrolytic layer is enhanced decreasing the contact resistance thereof. As a result, the equivalent series resistance in the high frequency regions is notably decreased.

In the solid electrolytic capacitor, as the cathode, a carbon layer may be formed in addition to the mixed layer. Such a carbon layer is formed between the electrolytic layer and the mixed layer.

In a case where the carbon layer is formed on the electrolytic layer as mentioned above and the mixed layer containing the first material consisting of the silver

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particles having the median diameter of not less than 2 μ m, the second material consisting of the conducting carbon particles and/or the silver particles having the median diameter of 1 μm or less and the biding agent is formed on the carbon layer, the particles of the second material consisting of the conducting carbon particles and/or the silver particles having the median diameter of 1 μm or less enter the spaces between the particles of the first material consisting of the silver particles having the median diameter of not less than 2 μm in the mixed layer, so that the conductivity in the mixed layer is improved and the adhering property between the mixed layer and the carbon layer is enhanced decreasing the contact resistance. As a result, the equivalent series resistance in high frequency regions is notably decreased.

Further, in the mixed layer of the solid electrolytic capacitor, when an amount of the second material consisting of the conducting carbon particles and/or the silver particles having the median diameter of 1 μm or less is insufficient, the particles of the second material consisting of the conducting carbon particles and/or the silver particles having the median diameter of 1 μm or less do not sufficiently enter the spaces between the particles of the first material consisting of the silver particles having the median diameter of not less

than 2 μm, so that it becomes difficult to obtain the above mentioned results. On the other hand, when the amount of the second material is excessive, the amount of the first material having a larger particle diameter becomes insufficient. As a result, electricity moves passing through a lot of contact areas, and the contact resistance between particles is increased causing increase in the equivalent series resistance. In view of the above, the amount of the second material based on a total amount of the first material and the second material is preferably set in a range of 0.5 to 40 wt%, and more preferably in a range of 3 to 40 wt%.

In the solid electrolytic capacitor, it is difficult to obtain the silver particles having the median diameter of 1 μm or less to be used in the mixed layer by grinding. Therefore, it is preferable to reduce silver oxide particles having the median diameter of 1 μm or less to obtain silver particles having the median diameter of 1 μm or less.

In order to obtain the mixed layer containing the silver particles having the median diameter of 1 μm or less, the silver oxide particles having the median diameter of 1 μm or less are contained in the mixed layer and then the silver oxide particles are reduced.

In a case where the silver oxide particles having the median diameter of 1 μm or less are contained in the mixed layer and reduced, as a method of reduction, for example, heat-treatment at not less than 160°C is preferable.

Further, in the solid electrolytic capacitor, when the contact area between the silver particles of the first material and the silver particles of the second material is enlarged, the conductivity in the mixed layer is enhanced and the equivalent series resistance is decreased. In order to obtain such a result, it is preferable to use scale-shaped silver particles of which ratio of a thickness to a length is very small as the silver particles of the first material and the second material.

Usable scale-shaped silver particles as the first material are the scale-shaped silver particles having a median in a maximum length of not less than 2 μm and the usable scale-shaped silver particles as the second material are the scale-shaped silver particles having the median in the maximum length of 1 μm or less. The maximum length in the silver particles is a length of a line drawn maximumly between two points on the periphery of the particles. The median in the maximum length is a length of a cumulated point on the cumulated distribution curve of the maximum length of these particles becoming 50%.

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When a ratio of the maximum length L to thickness d (L/d) in each of the scale-shaped silver particles is too small, it becomes difficult to further decrease the equivalent series resistance by enlargement of the contact areas between the silver particles of the first material and silver particles of the second material. On the other hand, when the aforementioned ratio (L/d) is too large, an amount of the binding agent covering surfaces of the silver particles becomes excessive, so that the equivalent series resistance is increased. In view of the above, it is preferable to use scale-shaped silver particles having the ratio of the maximum length L to the thickness d (L/d) set in a range of 4 to 100.

As the same as the aforementioned solid electrolytic capacitor, in both cases where the scale-shaped silver particles having the median in the maximum length of not less than 2 μm are used as the first material and the scale-shaped silver particles having the median in the maximum length of 1 μm or less are used as the second material, when the amount of the second material in the mixed layer is insufficient, the particles of the second material do not sufficiently enter the spaces between the particles of the first material, so that the aforementioned results can not be obtained. On the other hand, when the amount of the second material is excessive, the amount of

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the first material becomes insufficient and electricity moves passing through a lot of contact areas, resulting in increase in the contact resistance and the equivalent series resistance in high frequency regions. In view of the above, the amount of the second material based on the total amount of the first material and the second material is preferably set in a range of 0.5 to 40 wt%, more preferably in a range of 3 to 40 wt%.

Further, as the same as the silver particles having the median diameter of 1 μm or less, it is difficult to obtain the scale-shaped silver particles having the median in the maximum length of 1 μm or less by grinding. Therefore, it is preferable to reduce the silver oxide particles having the median in the maximum length of 1 μm or less to obtain the silver particles having the median in the maximum length of 1 μm or less.

Further, in order to obtain the mixed layer containing the scale-shaped silver particles having the median in the maximum length of 1 μm or less, the silver oxide particles having the median in the maximum length of 1 μm or less are contained in the mixed layer and then the silver oxide particles are reduced.

In a case where the scale-shaped silver oxide particles having the median in the maximum length of 1 μm or less are contained in the mixed layer and reduced, as

the method for the reduction, for example, the heat-treatment at not less than 160°C is preferable.

As the conducting carbon particles in the second material, for example, carbon black or graphite can be used. In particular, it is preferable to use a mixture of carbon black and graphite.

As the binding agent for the mixed layer, it is possible to use well-known binding agents which has conventionally used. In particular, it is preferable to use at least one resin selected from polyimide resin, epoxy resin and polyester resin. In the case of using at least one resin selected from polyimide resin, epoxy resin and polyester resin as the binding agent, the adhesive characteristics between the carbon layer and the mixed layer is further enhanced and the equivalent series resistance in the high frequency regions is further decreased in a first solid electrolytic capacitor wherein the carbon layer is formed, and the adhesive characteristics between the electrolytic layer and the mixed layer is further enhanced and the equivalent series resistance in high frequency regions is further decreased in a second solid electrolytic capacitor wherein the carbon layer is not formed.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1 is a sectional view illustrating a solid electrolytic capacitor according to Embodiment 1 of the invention;

Fig.2 is a sectional view illustrating a solid electrolytic capacitor according to Embodiment 2 of the invention;

Fig.3 is a sectional view illustrating a solid electrolytic capacitor fabricated in Comparative Example 1; and

Fig.4 is a sectional view illustrating a solid electrolytic capacitor fabricated in Comparative Example 2.

BEST MODES FOR CARRYING OUT THE INVENTION

A solid electrolytic capacitor according to Embodiments of the invention will be described hereinbelow in details with reference to the accompanying drawings. (Embodiment 1)

As shown in Figure 1, a solid electrolytic capacitor according to Embodiment 1 has the following structure. An anode 1 formed of at least one metal selected from tantalum, niobium, titanium and tungsten is anodized to form a dielectric layer 2 of an oxide on a surface thereof, an electrolytic layer 3 comprising such as conducting polymer and manganese dioxide is formed on the dielectric

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layer 2, and a cathode 4 is formed on the electrolytic layer 3.

In the solid electrolytic capacitor of Embodiment 1, a carbon layer 4a is formed as the cathode 4 on the electrolytic layer 3 and a mixed layer 4b containing a first material consisting of silver particles having a median diameter of not less than 2 μm, a second material consisting of conducting carbon particles and/or silver particles having a median diameter of 1μm or less and a binding agent is formed on the carbon layer 4a.

It is possible to use scale-shaped silver particles having the median in the maximum length of not less than 2 μm as the first material instead of the silver particles having the median diameter of not less than 2 μm. Also, it is possible to use the scale-shaped silver particles having the median in the maximum length of 1 μm or less as the second material instead of the silver particles having the median diameter of 1 μm or less.

(Embodiment 2)

As shown in Figure 2, a solid electrolytic capacitor according to Embodiment 2 has the following structure. The anode 1 formed of at least one metal selected from tantalum, niobium, titanium and tungsten is anodized to form the dielectric layer 2 of an oxide on the surface thereof, the electrolytic layer 3 formed of such as

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conducting polymer and manganese dioxide is formed on the dielectric layer 2, and the cathode 4 is formed on the electrolytic layer 3.

In the solid electrolytic capacitor of the Embodiment 2, the carbon layer 4a is not formed as the cathode 4 on the electrolytic layer 3, only the mixed layer 4b containing the first material consisting of the silver particles having the median diameter of not less than 2 μ m, the second material consisting of the conducting carbon particles and/or the silver particles having the median diameter of 1 μm or less and the binding agent is formed.

In the solid electrolytic capacitor of Embodiment 2, it is possible to use scale-shaped silver particles having a median in a maximum length of not less than 2 μm as the first material instead of the silver particles having the median diameter of not less than 2 μm. Also, it is possible to use the scale-shaped silver particles having the median in the maximum length of 1 μm or less as the second material instead of the silver particles having the median diameter of 1 μm or less.

(Examples)

Hereinafter, a solid electrolytic capacitor according to examples of the invention will specifically be described while comparative examples will be cited to demonstrate that equivalent series resistance in high

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frequency regions in the inventive solid electrolytic capacitor of examples is notably decreased. It is to be noted that the solid electrolytic capacitor of the invention should not be limited to the following examples thereof and suitable changes and modifications may be made thereto within the scope of the invention.

(Example A1)

A solid electrolytic capacitor of Example A1 has the same structure of the solid electrolytic capacitor of Embodiment 1 as described above.

In the solid electrolytic capacitor according to Example A1, an anode formed of tantalum sintered body was anodized to form a dielectric layer 2 of an oxide film on a surface thereof, an electrolytic layer 3 consisting of polypyrrole of a conducting polymer obtained by electrolytic polymerization and so on was formed on the dielectric layer 2, and a cathode 4 was formed on the electrolytic layer 3.

In forming the cathode 4 on the electrolytic layer 3, a carbon paste prepared by mixing graphite (5 wt%), water (90 wt%) and carboxymethyl cellulose as a binding agent (5 wt%) was coated on the electrolytic layer 3 and dried at a temperature of 150°C for 30 minutes to form a carbon layer 4a on the electrolytic layer 3.

On the other hand, a paste for the mixed layer was prepared by admixing 88 parts by weight of a mixture wherein silver particles of nearly spherical form having a median diameter of 3 μm and silver oxide (I) Ag_2O particles of nearly spherical form having a median diameter of 0.5 μm were mixed in a weight ratio of 95:5 with 5 parts by weight of polyamideimide which is one of polyimide resin as the binding agent and 7 parts by weight of γ-butyrolactone as a solvent.

Next, the paste for the mixed layer was coated on the carbon layer 4a and dried at 160°C for 30 minutes reducing the silver oxide (I) Ag_2O particles to form the mixed layer 4b containing the silver particles having the median diameter of 3 μm and the silver particles having the median diameter of 0.5 μm bound by polyamideimide.
(Example A2)

In a solid electrolytic capacitor of Example A2, silver oxide (II) AgO particles of nearly spherical form having a median diameter of 0.5 μm was used instead of the silver oxide (I) Ag_2O particles of nearly spherical form having the median diameter of 0.5 μm for preparing the paste for the mixed layer of the solid electrolytic capacitor of Example A1. Except for the above, the same procedure as in Example 1 was used to form the mixed layer 4b containing the silver particles having the median

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diameter of 3 μm and the silver particles having the

median diameter of 0.5 μm bound by polyamideimide.

(Example A3)

     In a solid electrolytic capacitor of Example A3,

acetylene black which is one of carbon black having a

median diameter of 0.05 μm was used instead of the Ag_2O

particles having the median diameter of 0.5 μm for

preparing the paste for the mixed layer of the solid

electrolytic capacitor of Example A1. Except for the

above, the same procedure as in Example A1 was used to form

the mixed layer 4b containing the silver particles having

the median diameter of 3 μm and acetylene black having the

median diameter of 0.05 μm bound by polyamideimide.

(Example A4)

     In a solid electrolytic capacitor of Example A4, a

mixture wherein the silver particles of nearly spherical

form having the median diameter of 3 μm, the Ag_2O

particles of nearly spherical form having the median

diameter of 0.5 μm and acetylene black having the median

diameter of 0.05 μm were mixed in a weight ratio of

95:2.5:2.5 was used for preparing the paste for the mixed

layer of the solid electrolytic capacitor of Example A1.

Except for the above, the same procedure as in Example A1

was used to form the mixed layer 4b containing the silver

particles having the median diameter of 3 μm, the silver

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particles having the median diameter of 0.5 μm and acetylene black having the median diameter of 0.05 μm bound by polyamideimide.

(Example B1)

A solid electrolytic capacitor of Example B1 has the same structure of the solid electrolytic capacitor of Embodiment 2 as described above.

In a solid electrolytic capacitor of Example B1, in forming the cathode 4 of the solid electrolytic capacitor of Example A1, the carbon layer 4a was not formed on the electrolytic layer 3 consisting of polypyrrole. Except for the above, the same procedure as in Example A1 was used to form the cathode 4 consisting of the mixed layer 4b containing the silver particles having the median diameter of 3 μm and the silver particles having the median diameter of 0.5 μm bound by polyamideimide on the electrolytic layer 3.

(Comparative Example 1)

In a solid electrolytic capacitor of Comparative Example 1, a silver paste prepared by admixing 88 parts by weight of the silver particles of nearly spherical form having the median diameter of 3 μm with 5 parts by weight of polyamideimide and 7 parts by weight of γ-butyrolactone as the solvent was used instead of the paste for the mixed layer used in the solid electrolytic capacitor of Example

A1. Except for the above, the same procedure as in Example A1 was used to form a silver layer 4c wherein the silver particles having the median diameter of 3 μm were bound by polyamideimide as shown in Fig. 3.

(Comparative Example 2)

In a solid electrolytic capacitor of Comparative Example 2, the same procedure as in Example A3 was used to form the mixed layer 4b containing the silver particles of nearly spherical form having the median diameter of 3 μm and acetylene black having the median diameter of 0.05 μm bound by polyamideimide. Then, as shown in Fig.4, the silver paste prepared by admixing 88 parts by weight of the silver particles having the median diameter of 3 μm with 5 parts by weight of polyamideimide and 7 parts by weight of γ-butyrolactone as the solvent was coated on the mixed layer 4b and dried at 150°C for 30 minutes to form the silver layer 4c on the mixed layer 4b.

The resultant solid electrolytic capacitors of Examples A1 to A4, Example B1 and Comparative Examples 1 and 2 were each determined for the equivalent series resistance (ESR) by means of an equivalent series resistance meter at a frequency of 100 kHz. An index number of the equivalent series resistance (ESR) of each of the solid electrolytic capacitors was determined on a basis of the equivalent series resistance (ESR) of the solid

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electrolytic capacitor of Example A1 defined as 100. The
results are listed in Table 1 as below.

[Table 1]

	EXAMPLE					COMPARATIVE EXAMPLE	
	A1	A2	A3	A4	B1	1	2
ESR	100	100	102	97	102	160	150

As is apparent from the table, each of the solid
electrolytic capacitors of Examples A1 to A4 wherein the
respective carbon layer 4a and the mixed layer 4b
containing the first material consisting of the silver
particles having the median diameter of not less than 2 μm
and the second material consisting of the conducting carbon
particles and/or silver particles having the median
diameter of 1 μm or less were formed on the electrolytic
layer 3 and the solid electrolytic capacitor of Example B1
wherein the carbon layer 4a was not formed and the mixed
layer 4b was formed directly on the electrolytic layer 3
presented a notably decreased ESR as compared with the
solid electrolytic capacitor of Comparative Example 1
wherein the silver layer 4c containing the silver particles
having the median diameter of 3 μm was formed instead of
the mixed layer 4b and the solid electrolytic capacitor of
Comparative Example 2 wherein the silver layer 4c
containing only the silver particles having the median
diameter of 3 μm was formed on the mixed layer 4b.

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According to a comparison among the solid electrolytic capacitors of Examples A1 to A4 and Example B1, the solid electrolytic capacitors using the second material containing the silver particles having the median diameter of 1 μm or less presented a decreased ESR as compared with the solid electrolytic capacitor of Example A3 using the second material containing only acetylene black of the conducting carbon particles. In particular, the ESR in the solid electrolytic capacitor of A4 using the second material containing both the silver particles having the median diameter of 1 μm or less and acetylene black of the conducting carbon particles was further decreased.

(Examples A5 and A6)

The same procedure as in Example A3 was used to fabricate each of solid electrolytic capacitors of Example A5 and A6, except that a type of the conducting carbon particles contained in the mixed layer 4b was changed.

As the conducting carbon particles, graphite having the median diameter of 5 μm was used in Example A5 and a mixture prepared by mixing acetylene black having the median diameter of 0.05 μm and graphite having the median diameter of 5 μm in a weight ratio of 1:1 was used in Example A6.

In the same manner as above, the resultant solid electrolytic capacitors of Examples A5 and A6 were each

determined for the equivalent series resistance (ESR) at the frequency of 100 kHz. Then, an index number of the equivalent series resistance (ESR) of each of the solid electrolytic capacitors of Examples A5 and A6 was determined on the basis of the equivalent series resistance (ESR) of the solid electrolytic capacitor of Example A3 defined as 100. The results are listed in Table 2 as below.

[TABLE 2]

	TYPE OF CONDUCTING CARBON PARTICLES	ESR
EXAMPLE A3	acetylene black	100
EXAMPLE A5	graphite	105
EXAMPLE A6	acetylene black + graphite	97

As is apparent from the table, as the solid electrolytic capacitor of Example A3 using acetylene black as the conducting carbon particles contained in the mixed layer 4b, each of the solid electrolytic capacitors of Examples A5 and A6 using graphite or the mixture of acetylene black and graphite presented a notably decreased ESR as compared with the solid electrolytic capacitors of Comparative Examples 1 and 2.

Further, the solid electrolytic capacitors wherein acetylene black having a small particle diameter was contained as the conducting carbon particles in the mixed layer 4b presented a decreased ESR as compared with the

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solid electrolytic capacitor of Example A5 wherein only graphite having a large particle diameter was contained as the conducting carbon materials in the mixed layer 4b. In particular, the ESR in the solid electrolytic capacitor of Example A6 using the mixture of acetylene black having the small particle diameter and graphite having the large particle diameter was further decreased.

(Examples A7 and A8 and Comparative Examples 3 and 4)

The same procedure as in Example A1 was used to fabricate each of solid electrolytic capacitors of Examples A7 and A8 and Comparative Examples 3 and 4, except that the median diameter of the Ag_2O particles to be added to the paste for the mixed layer was changed and the median diameter of the silver particles having a small particle diameter to be mixed to the silver particles having the median diameter of 3 μm in the mixed layer 4b was changed.

Example A7 used Ag_2O particles having a median diameter of 0.1 μm, Example A8 used Ag_2O particles having a median diameter of 1.0 μm, Comparative Example 3 used Ag_2O particles having a median diameter of 1.5 μm and Comparative Example 4 used Ag_2O particles having a median diameter of 2.0 μm. When the Ag_2O particles were dried at 160°C for 30 minutes and reduced into silver particles in the same manner as above, the silver particles having the

same median diameter as before reduction were contained in the mixed layer.

In the same manner as above, the resultant solid electrolytic capacitors of Examples A7 and A8 and Comparative Examples 3 and 4 were each determined for the equivalent series resistance (ESR) at the frequency of 100 kHz. Then, an index number of the equivalent series resistance (ESR) of each of the solid electrolytic capacitors of Examples A7 and A8 and Comparative Examples 3 and 4 was determined on the basis of the equivalent series resistance (ESR) of the solid electrolytic capacitor of Example A1 defined as 100. The results are listed in Table 3 as below.

[TABLE 3]

	AVERAGE PARTICLE DIAMETER OF SILVER OXIDE(I) Ag_2O (μm)	ESR
EXAMPLE A7	0.1	98
EXAMPLE A1	0.5	100
EXAMPLE A8	1	110
COMPARATIVE EXAMPLE 3	1.5	150
COMPARATIVE EXAMPLE 4	2	160

As is apparent from the table, in each of the solid electrolytic capacitors of Examples A1, A7 and A8 using silver particles having the median diameter of 1 μm or less as the silver particles having the small particle

diameter to be mixed with the silver particles having the median diameter of 3 μm in the mixed layer 4b, the ESR was notably decreased as compared with the solid electrolytic capacitors of Comparative Examples 3 and 4 using silver particles having the median diameter of more than 1 μm as the silver particles having the small particle diameter to be mixed with the silver particles having the median diameter of 3 μm.

(Examples A9 to A18)

In Examples A9 to A18, the same procedure as in Example A4 was used to form the mixed layer 4b containing the mixture of the silver particles having the median diameter of 3 μm, the Ag$_2$O particles having the median diameter of 0.5 μm and acetylene black having the median diameter of 0.05 μm, except the weight ratio thereof was changed.

Each weight ratio was set in 99.75:0.125:0.125 in Example A9, 99.5:0.25:0.25 in Example A10, 99:0.5:0.5 in Example A11, 98:1:1 in Example A12, 97:1:2 in Example A13, 90:5:5 in Example A14, 80:15:5 in Example A15, 60:35:5 in Example A16, 55:40:5 in Example A17 and 50:45:5 in Example A18. Except for the above, the same procedure as in Example A4 was used to fabricate each of the solid electrolytic capacitors of Example A9 to A18.

In the resultant solid electrolytic capacitors of Examples A9 to A18, a weight ratio W (Wt%) of the second material based on a total amount of the first material consisting of the silver particles having the median diameter of 3 μm and the second material consisting of the silver particles reduced from the Ag_2O particles having the median diameter of 0.5 μm and acetylene black was almost the same as the aforesaid weight ratio in mixing. Each weight ratio W was 0.25 wt% in Example A9, 0.5 wt% in Example A10, 1 wt% in Example A11, 2 wt% in Example A12, 3 wt% in Example A13, 10 wt% in Example A14, 20 wt% in Example A15, 40 wt% in Example A16, 45 wt% in Example A17, 50 wt% in Example A18 and 5 wt% in Example A4.

In the same manner as above, the resultant solid electrolytic capacitors of Examples A9 to A18 were each determined for the equivalent series resistance (ESR) at the frequency of 100 kHz. Then, an index number of the equivalent series resistance (ESR) of each of the solid electrolytic capacitors of Examples A9 to A18 was determined on the basis of the equivalent series resistance (ESR) of the solid electrolytic capacitor of Example A4 defined as 100. The results are listed in Table 4 as below.

[TABLE 4]

	WEIGHT RATIO			W (wt%)	ESR
	3 μm SILVER PARTICLES	0.5 μm SILVER OXIDE(I) Ag$_2$O PARTICLES	ACETYLENE BLACK		
EXAMPLE A9	99.75	0.125	0.125	0.25	145
EXAMPLE A10	99.5	0.25	0.25	0.5	115
EXAMPLE A11	99	0.5	0.5	1	105
EXAMPLE A12	98	1	1	2	105
EXAMPLE A13	97	1	2	3	100
EXAMPLE A4	95	2.5	2.5	5	100
EXAMPLE A14	90	5	5	10	102
EXAMPLE A15	80	15	5	20	102
EXAMPLE A16	60	35	5	40	103
EXAMPLE A17	55	40	5	45	135
EXAMPLE A18	50	45	5	50	140

As is apparent from the table, each of the solid electrolytic capacitors of Examples A4 and A10 to A16 wherein the weight ratio W of the second material based on the total amount of the first material consisting of the silver particles having the median diameter of 3 μm and the second material consisting of the silver particles having the median diameter of 0.5 μm and acetylene black was set in a range of 0.5 to 40 wt% presented a notably decreased ESR as compared with the solid electrolytic capacitor of Example A9 wherein the weight ratio W was 0.25 wt% and the solid electrolytic capacitors of Examples A17

and A18 wherein the weight ratio W was more than 40 wt%.
In particular, the ESR in each of the solid electrolytic
capacitors of Example A4 and Examples A13 to A16 wherein
the weight ratio W was in a range of 3 to 40 wt% was
further decreased.

(Examples A19, A20 and Comparative Example 5)

The same procedure as in Example A1 was used to
fabricate each of solid electrolytic capacitors of Examples
A19, A20 and Comparative Example 5, except that a drying
temperature for drying the paste for the mixed layer was
changed. Each drying temperature was set to 170°C in
Example A19, 180°C in Example A20 and 150°C in Comparative
Example 5. In a case where the drying temperature for
drying the paste for the mixed layer was set to 150°C as in
Comparative Example 5, the Ag_2O particles in the paste for
the mixed layer were not sufficiently reduced to the silver
particles.

In the same manner as above, the resultant solid
electrolytic capacitors of Examples A19, A20 and
Comparative Example 5 were each determined for the
equivalent series resistance (ESR) at the frequency of 100
kHz. Then, an index number of the equivalent series
resistance (ESR) of each of the solid electrolytic
capacitors of Examples A19, A20 and Comparative Example 5
was determined on the basis of the equivalent series

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resistance (ESR) of the solid electrolytic capacitor of Example A1 defined as 100. The results are listed in Table 5 as below.

[TABLE 5]

	DRYING TEMPERATURE (°C)	ESR
COMPARATIVE EXAMPLE 5	150	150
EXAMPLE A1	160	100
EXAMPLE A19	170	100
EXAMPLE A20	180	100

As is apparent from the table, each of the solid electrolytic capacitors of Examples A1, A19 and A20 wherein the drying temperature for drying the paste for the mixed layer was set to not less than 160°C to reduce the Ag_2O particles sufficiently to the silver particles presented a notably decreased ESR as compared with the solid electrolytic capacitor of Comparative Example 5 wherein the drying temperature was set to 150°C and the Ag_2O particles in the mixed layer were not sufficiently reduced to silver particles.

(Examples A1a, A1b and A1c and Comparative Examples 1a, 1b and 1c)

The same procedure as in Example A1 was used to fabricate each of solid electrolytic capacitors of Examples A1a, A1b, and A1c, except that a type of the binding agent for preparing the paste for the mixed layer was changed.

Example A1a used an epoxy resin as the binding agent and diethylene glycol monobutyl ether as the solvent. Example A1b used a polyester resin as the binding agent and cyclohexanone as the solvent. Example A1c used a phenolic resin as the binding agent and propylene glycol as the solvent. Except for the above, the same procedure as in Example A1 was used to fabricate each of the solid electrolytic capacitors of Examples A1a, A1b and A1c.

The same procedure as in Comparative Example 1 was used to fabricate each of solid electrolytic capacitors of Comparative Examples 1a, 1b, and 1c, except that a type of the binding agent for preparing the paste for the mixed layer was changed.

Comparative Example 1a used the epoxy resin as the binding agent and diethylene glycol monobutyl ether as the solvent. Comparative Example 1b used the polyester resin as the binding agent and cyclohexanone as the solvent. Comparative Example 1c used the phenolic resin as the binding agent and propylene glycol as the solvent. Except for the above, the same procedure as in Comparative Example 1 was used to fabricate each of the solid electrolytic capacitors of Comparative Examples 1a, 1b and 1c.

In the same manner as above, the resultant solid electrolytic capacitors of Examples A1a, A1b and A1c and Comparative Examples 1a, 1b and 1c were each determined for

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the equivalent series resistance (ESR) at the frequency of
100 kHz. Then, an index number of the equivalent series
resistance (ESR) of each of the solid electrolytic
capacitors of Examples A1a, A1b and A1c and Comparative
Examples 1a, 1b and 1c was determined on the basis of the
equivalent series resistance (ESR) of the solid
electrolytic capacitor of Example A1 defined as 100. The
results are listed in Table 6 as below.

[TABLE 6]

	TYPE OF BINDING AGENT	ESR
EXAMPLE A1	polyamideimide	100
EXAMPLE A1a	epoxy resin	105
EXAMPLE A1b	polyester resin	105
EXAMPLE A1c	phenolic resin	160
COMPARATIVE EXAMPLE 1	polyamideimide	160
COMPARATIVE EXAMPLE 1a	epoxy resin	165
COMPARATIVE EXAMPLE 1b	polyester resin	165
COMPARATIVE EXAMPLE 1b	phenolic resin	200

As is apparent from the table, even in a case where
the type of the biding agent was changed, each of the solid
electrolytic capacitors of Examples A1a, A1b and A1c
presented a notably decreased ESR as compared with the
solid electrolytic capacitors of Comparative Examples 1a,
1b and 1c.

In a comparison of values of the ESR according to the type of the biding agent, in the case of using polyamideimiede(polyimide resin), epoxy resin or polyester resin, the ESR was notably decreased as compared with the case of using phenolic resin.

(Examples C1 to C3)

The same procedure as in Example A4 was used to fabricate each of solid electrolytic capacitors of Examples C1 to C3, except that the first material consisting of the silver particles of nearly spherical form having the median diameter of 3 μm and the second material consisting of the silver oxide particles of nearly spherical form having the median diameter of 0.5 μm contained in the mixed layer were changed.

In Example C1, scale-shaped silver particles wherein the median in the maximum length L was 3 μm and the ratio of the maximum length L to the thickness d (L/d) was 20 were used as the first material and scale-shaped silver particles wherein the median in the maximum length was 0.5 μm and the ratio of the maximum length L to the thickness d (L/d) was 20 were used as the second material.

In Example C2, the scale-shaped silver particles wherein the median in the maximum length L was 3 μm and the ratio of the maximum length L to the thickness d (L/d) was 20 were used as the first material and the silver

particles of nearly spherical form having the median diameter of 0.5 μm used in Example A4 were used as the second material.

In Example C3, the silver particles of nearly spherical form having the median diameter of 3 μm used in Example A4 were used as the first material and scale-shaped silver particles wherein the median in the maximum length L was 0.5 μm and the ratio of the maximum length L to the thickness d (L/d) was 20 were used as the second material.

In the same manner as above, the resultant solid electrolytic capacitors of Examples C1 to C3 were each determined for the equivalent series resistance (ESR) at the frequency of 100 kHz. Then, an index number of the equivalent series resistance (ESR) of each of the solid electrolytic capacitors of Examples C1 to C3 was determined on the basis of the equivalent series resistance (ESR) of the solid electrolytic capacitor of Example A4 defined as 100. The results are listed in Table 7 as below.

[TABLE 7]

	SILVER PARTICLES OF FIRST MATERIAL	SILVER PARTICLES OF SECOND MATERIAL	ESR
EXAMPLE C1	scale-shaped	scale-shaped	65
EXAMPLE C2	scale-shaped	nearly spherical form	93
EXAMPLE C3	nearly spherical form	scale-shaped	95
EXAMPLE A4	nearly spherical form	nearly spherical form	100

As is apparent from the table, each of the solid electrolytic capacitors of Examples C1 to C3 using the scale-shaped silver particles at least either in the first material or in the second material presented a notably decreased ESR as compared with the solid electrolytic capacitor of Examples A4 using the silver particles of nearly spherical form in both of the first material and the second material. In particular, the ESR in the solid electrolytic capacitor of Example C1 using the scale-shaped silver particles in both of the first material and the second material was further decreased.

(Examples C4 to C7)

In Examples C4 to C7, the scale-shaped silver particles wherein the median in the maximum length L was 3 μm were used as the first material and the scale-shaped silver particles wherein the median in the maximum length L was 0.5 μm were used in the same manner as Example C1. However, the ratio of the maximum length L to the thickness

d (L/d) in the scale-shaped silver particles of the first

material and the second material was changed. Except for

the above, the same procedure as in Example C1 was used to

fabricate each of solid electrolytic capacitors of Examples

C4 to C7.

In Example C4, scale-shaped silver particles wherein

the ratio of the maximum length L to the thickness d (L/d)

was 4 were used in the first material and the second

material. In Example C5, scale-shaped silver particles

wherein the ratio of the maximum length L to the thickness

d (L/d) was 50 in the first material and the second

material were used. In Example C6, scale-shaped silver

particles wherein the ratio of the maximum length L to the

thickness d (L/d) was 100 were used in the first material

and the second material. In Example C7, scale-shaped

silver particles wherein the ratio of the maximum length L

to the thickness d (L/d) was 120 were used in the first

material and the second material.

In the same manner as above, the resultant solid

electrolytic capacitors of Examples C4 to C7 were each

determined for the equivalent series resistance (ESR) at

the frequency of 100 kHz. Then, an index number of the

equivalent series resistance (ESR) of each of the solid

electrolytic capacitors of Examples C4 to C7 was determined

on the basis of the equivalent series resistance (ESR) of

the solid electrolytic capacitor of Example A4 defined as
100. The results are listed in Table 8 as below.

[TABLE 8]

	SILVER PARTICLES OF FIRST MATERIAL		SILVER PARTICLES OF SECOND MATERIAL		ESR
	SHAPE	L/d	SHAPE	L/d	
EXAMPLE C4	scale-shaped	4	scale-shaped	4	70
EXAMPLE C1	scale-shaped	20	scale-shaped	20	65
EXAMPLE C5	scale-shaped	50	scale-shaped	50	72
EXAMPLE C6	scale-shaped	100	scale-shaped	100	74
EXAMPLE C7	scale-shaped	120	scale-shaped	120	92
EXAMPLE A4	nearly spherical form	about 1	nearly spherical form	about 1	100

As is apparent from the table, each of the solid
electrolytic capacitors of Examples C1 and C4 to C6 using
the scale-shaped silver particles wherein the ratio of the
maximum length L to the thickness d (L/d) in the first
material and the second material was in the range of 4 to
100 presented a notably decreased ESR.

INDUSTRIAL APPLICABILITY

According to the solid electrolytic capacitor of the
invention as described above, the mixed layer containing
the first material consisting of the silver particles
having the median diameter of not less than 2 μm, the

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second material consisting of the conducting carbon particles and/or the silver particles having the median diameter of 1 μm or less and the biding agent is formed as the cathode on the electrolytic layer, so that the particles of the second material consisting of the conducting carbon particles and/or the silver particles having the median diameter of 1 μm or less enter the spaces between the particles of the first material consisting of the silver particles having the median diameter of not less than 2 μm in the mixed layer. As a result, the conductivity in the mixed layer is improved, the adhering property between the mixed layer and the electrolytic layer is enhanced decreasing the contact resistance thereof, and the equivalent series resistance in the high frequency regions is notably decreased.

Further, in the solid electrolytic capacitor, in a case where the carbon layer is formed between the electrolytic layer and the mixed layer, the adhering property between the mixed layer and the carbon layer is enhanced decreasing the contact resistance thereof, and the equivalent series resistance in the high frequency regions is further decreased.

Furthermore, in the solid electrolytic capacitor, the scale-shaped silver particles of which thickness to the length is very small are used in the first material and the

second material in the mixed layer, so that the contact area between the silver particles of the first material and the silver particles of the second material is enlarged, resulting in still further decrease in the equivalent series resistance in the high frequency regions.